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(19)

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(54) REINFORCED THERMOPLASTIC COMPOSITIONS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the Laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to reinforced thermoplastic compositions for molding and conversion to films, fibers, and sheets. Also contemplated are flame retardant and non-dripping forms of such compositions.

High molecular weight linear polyesters and copolyesters of glycols and terephthalic or isophthalic acid have been available for a number of years. These are described *inter alia* in Whinfield *et al*, U.S. Patent No. 2,465,319 and in Pengilly, U.S. Patent No. 3,047,539. These patents disclose that the polyesters are particularly advantageous as film and fiber formers.

The most commonly employed polyester prepared by these teachings, poly(ethylene terephthalate), has only fairly recently been widely accepted for use as a molding resin because of its relative brittleness in thick sections when crystallized from the melt. The problem was overcome by varying the crystal texture, e.g., by using two-step molding cycles or by including nucleating agents, and by molecular weight control. This permitted the marketing of injection-moldable poly(ethylene terephthalates) which typically, in comparison with other thermoplastics, offer a high degree of surface hardness and abrasion resistance, and lower surface friction. Solvent resistance is outstanding, making such compositions uniquely useful in the automotive and aircraft industries. Among the disadvantages of poly(ethylene terephthalate) in molding compositions are the relatively high cost of manufacture (because of the need to control crystal texture), a relatively low degree of moisture resistance, a rapid burning rate and a tendency to drip flaming resin while burning.

Surprisingly, it has been found that the need to employ nucleating agents or two stage molding cycles to avoid brittleness in thick molded sections is obviated if higher homologs of poly(ethylene terephthalate) are mixed with it or substituted for it. For example, within the broad disclosure of the Whinfield *et al* and Pingilly patents there exists a family of polyester resins which are normally crystalline and which rapidly crystallize from the melt. These crystallize so rapidly, in fact, that standard injection molding cycles can be used and there is no need to include nucleating agents in the formulation. Parts molded from such polyesters, in contrast to those of poly(ethylene terephthalate) alone, have good impact strength in thick sections.

The rapidly crystallizable higher homologs comprise generally polyester resins which are poly(alkylene terephthalates, isophthalates or mixed terephthalates and isophthalates), wherein the alkylene groups contain from 3 to 10, and especially 3 to 6, carbon atoms.

Simultaneously with the development of injection molding grades of

poly(ethylene terephthalate) resins, fiber glass reinforced compositions were also provided. See Furukawa *et al.*, U.S. Patent No. 3,368,995. These injection moldable compositions provided all of the advantages of unfilled polyesters and, also, because of the glass reinforcement, the molded articles had higher rigidity, yield strength, modulus and impact strength.

However, because they used poly(ethylene terephthalate) the Furukawa et al compositions required two stage molding or the use of nucleating agents to avoid embrittled thickly molded sections. Moreover, they retained the disadvantages inherent in polyesters generally, having a relatively high cost of manufacture and formulation, and low degree of moisture resistance, high flammability and a tendency to drip while burning.

Although substitution of the rapidly crystallizable higher homologs of poly(ethylene terephthalate) would be expected to overcome the need for two-stage molding cycles or nucleating agents, such compositions, in common with those described by Furukawa *et al*, would still be expensive, unstable to moisture, flammable and would drip while burning. While resistant to gasoline, jet fuels, and hydraulic fluids, such compositions would be of limited utility in the automotive and aircraft industries because of their flammability. On the other hand, because of moisture sensitivity, their use in kitchens, laundries or ships would be limited.

This invention relates to a thermoplastic composition comprising a rapidly crystallizable polyester (as hereinafter defined) with at least one other polymer and a reinforcing filler. Without the filler component, great difficulty is experienced in processing the blend of two polymers. Surprisingly, as little as 2% by weight of reinforcing filler, such as glass, provides unexpected improvement in processability, surface appearance and physical properties.

Merely by way of illustration, the hydrolytic stability of poly(1,4-butylene terephthalate) will be enhanced according to this invention by forming a reinforced combination with polyolefins and the strength, rigidity, and resistance to heat distortion of polyolefins will be improved by forming a reinforced combination with poly (1,4-butylene terephthalate).

It is surprising and unexpected to find that such polyesters form useful combinations with a remarkably broad range of polymers. Usually, when such mixtures, including at least one highly crystallizable polymer, are molded and cooled, they are non-uniform and tend to delaminate (i.e. to separate into their individual components). In contrast to the expected behaviour, rapidly crystallizable polyesters have been found readily to form composites with crystalline, amorphous and partially crystalline and partially amorphous polymers and, after reinforcement, the resulting composites are easily moldable and extrudable into articles which are uniform and which do not delaminate. All of these characteristics of the new compositions of this invention indicate that an intercrystalline (i.e. homogeneous crystalline mixture) is formed between the polyester and the second co-blended polymer. In addition, the enhancement in strength of the composite is evidence that the reinforcing filler, e.g. a metal, ceramic, silica, quartz, asbestos, silicate, titanate, carbon black, clay or glass, is unexpectedly and strongly bonded into the combination.

This invention provides a reinforced thermoplastic composition that is rigid at temperatures of up to 90°F, which comprises a homogeneous crystalline normally rigid, reinforceable mixture of:

(a) at least one high molecular weight normally crystalline polyester resin which rapidly crystallizes from the melt (as hereinbefore defined);

(b) at least one high molecular weight normally crystalline, normally amorphous or normally partially crystalline and partially amorphous polymer of:

(i) at least one aliphatic ethylenically unsaturated monomer excluding propylene;

(ii) at least one difunctionally reactive compound which is polymerizable by self-condensation; and/or

(iii) at least two difunctionally reactive compounds which are polymerizble by polycondensation;

in the concentration range of from 1 to 99 parts by weight of (a) to 99 to 1 parts by weight of (b); and

(c) from 2 to 90% by weight, based on total composition, of a reinforcing filler for said homogeneous, crystalline, normally rigid, reinforceable mixture;

and when polymer (b) is a polyester, it is a wholly aromatic polyester and different from polyester (a).

With respect to the polyester resin component (a), there will be selected a

high molecular weight normally crystalline polycondensation product of a difunctional organic alcohol or reactive derivative thereof and a difunctional organic acid or a reactive derivative thereof. The difunctional alcohol and the difunctional acid can be wholly aliphatic or wholly aromatic or partially aliphatic and partially aromatic in character, the organic groups being straight chained, or branched, cyclic or polycyclic and containing from 2 to 20, preferably from 3 to 10, especially preferably from 3 to 6, carbon atoms. The organic groups can be unsubstituted or substituted with conventional substituents, such as alkyl, halogen, carboxyl, nitro, cyano, amido or imido groups.

While a wide variety of polyesters are suitable for this invention, it is important that they be normally crystalline, high enough in molecular weight to form films and fibers (although this is merely a measure of a suitable molecular weight and not a limitation on ultimate use) and, most importantly, rapidly crystallizable from the melt.

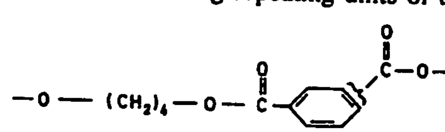
Polyesters which meet the criterion of being rapidly crystallizable from the melt will be those which can be injection molded into a mould having a temperature of from 160 to 175°F, preferably 170°F, when they themselves have a higher temperature than the mould in a standard, short cycle time and produce a rigid workpiece which is highly crystalline throughout. As is described in Furukawa *et al.* U.S. Patent No. 3,368,995, poly(ethylene terephthalate) will not produce such a workpiece because of its high crystalline melting point and low heat conductivity. Because such a polyester resin is not rapidly crystallizable, the outer part of the workpiece is amorphous, and the inner part, which is gradually cooled, is crystalline.

One convenient way to determine if a polyester is suitable for use in this invention is to injection mold it with the mold temperature of 160—175°F. in a standard short cycle, e.g., 10—90 seconds, into a workpiece about ⅛ inch thick. If the moulded article is rigid on removal from the mould and the inner and outer parts of the piece are uniformly milky or white and opaque and if the hardness, measured, e.g., with a Rockwell M tester, is uniform throughout, crystallization from the melt is rapid enough to be suitable. If, on the other hand, the workpiece is clear, transparent or semi-transparent (i.e., amorphous) on the outside and milky, white or opaque (i.e., crystalline) only on the inside; if the hardness is non-uniform throughout; if the workpiece is relatively soft on removal from the mould and brittle after cooling; or if uniformity can be achieved only by using a two stage molding cycle, or higher mold temperatures, e.g., 250—330°F. and long times, e.g., 90—400 sec., or by including a nucleating agent, e.g. carbon powders, metal salts or clays, then the polyester resin is not suitable for this invention.

Typical of the high molecular weight rapidly crystallizable polyester resins suitable for this invention are poly(alkylene terephthalates, isophthalates or mixed terephthalates and isophthalates), wherein the alkylene groups contain from 3 to 10 carbon atoms. They are available commercially or can be prepared by known techniques, such as by the alcoholysis of esters of the phthalic acid with a glycol and subsequent polymerization, by heating glycols with the free acids or with halide derivatives thereof, and similar processes. These are described in U.S. Patent No. 2,465,319 and U.S. Patent No. 3,047,539, and elsewhere.

Although the glycol portion of such typical polyesters can contain from 3 to 10 carbon atoms, e.g., 1,3-propylene, 1,4-butylene, 1,3-butylene, 1,2-propylene, 1,2-butylene, or 2,3-butylene, it is preferred that it contain 3 or 4 carbon atoms, in the form of linear mehylene chains.

Preferred polyesters are high molecular weight, polymeric 1,4-butylene glycol terephthalates or isophthalates having repeating units of the general formula



and mixtures of such esters, including copolyesters of terephthalic and isophthalic acids over the entire composition range.

Especially preferred polyesters are poly(1,4-butylene isophthalate) and poly(1,4-butylene terephthalate). Special mention is made of the latter because it is easy to prepare from readily available materials and crystallizes at an especially rapid rate.

Illustratively, sufficiently high molecular weight polyesters of the preferred type will have an intrinsic viscosity of at least 0.2 and preferably 0.4 deciliters/gram as measured in *o*-chlorophenol, a 60/40 phenol-tetrachloroethane mixture or a similar solvent at 25—30°C. The upper limit is not critical, but will generally be 1.5 dl./g. Especially preferred polyesters will have an intrinsic viscosity in the range from 0.5 to 1.3.

With respect to the co-blending polymer (b), these will be selected from one or more of high molecular weight normally crystalline, normally amorphous or normally partially crystalline and partially amorphous polymers (as described more fully below) which form with polyester component (a) a reinforceable combination with the concentration range of from 1 to 99 parts by weight of (a) to 99 to 1 parts by weight of (b).

It is to be understood that not all of the suitable polymers falling within the definition given for component (b) will form reinforceable combinations over the entire stated composition range. Numerous such polymers will form reinforceable combinations within only portions of this range, and all non-reinforceable combinations of polyesters and such polymers within the stated range are therefore not included in this invention. Non-reinforceable combinations are those which persons skilled in the art will readily recognize as failing to meet the criteria set out above, i.e., they may or may not combine each other when melted, but, when cooled, they will separate or delaminate, or lose physical properties.

The co-blending polymers (b) will form an intercrystalline normally rigid reinforceable composition with the normally crystalline polyester. Accordingly, the blending polymer component (b) can itself be normally crystalline, normally amorphous or mixed crystalline and amorphous. Crystallinity as used herein is that which arises from a state of molecular structure which denotes compactness of the molecular chains forming the polymer. It is attributable to the formation of solid crystals having a definite geometric form.

As is well understood by those skilled in the art, the same high molecular weight polymer, depending often on the way it is produced, can exist in wholly crystalline, wholly amorphous or partially crystalline and partially amorphous form. Merely by way of illustration, polymers of the same alpha olefin, e.g., poly(1-butene), have different steric structures, and depending on their steric configurations, they may be crystallizable or amorphous, or mixed.

Although as will be seen, polymer (b) can be either normally solid (i.e. rigid) or normally rubbery (i.e. non-rigid), the compositions of this invention are all normally rigid. Therefore, if polymer (b) is rubbery, the maximum amount used is that which ensures that the final composition will be rigid at temperatures of 75—90°F.

The polymer component (b) of this invention is a polymerization product of

(i) at least one aliphatic ethylenically unsaturated monomer excluding propylene, e.g., ethylene or an olefin of from 4 to 10 carbon atoms, e.g., butene-1, butadiene, methyl pentene, or decene-1, including vinyl monomers, such as a vinyl halide or vinylidene halide, for example, vinyl chloride, vinylidene chloride, or vinyl alkanoates, e.g., vinyl acetate, acrylic monomers such as acrylic acid, acrylic esters, alkyl methacrylates, acrylic nitriles, such as methacrylonitrile, and chlorinated polyethylene. (The term "aliphatic" is intended to exclude polymers and copolymers of vinyl aromatic compounds, e.g. styrene).

(ii) at least one difunctionally reactive compound which is polymerizable by self-condensation, such as formaldehyde, trioxymethylene, phenols, e.g., 2,6-dimethylphenol, siloxanes, lactams, e.g. caprolactam, or aromatic sulfides; and/or

(iii) at least two difunctionally reactive compounds which are polymerizable by polycondensation, such as a diamine, e.g., hexamethylenediamine, and a dicarboxylic acid, e.g., adipic acid, a polyorganosiloxane and an aromatic ester, a bis maleimide and an amine, or an ether of a bis phenol and a dichlorodiphenyl sulfone.

Component (b) can be, for instance a mixture of the polymerization products of (i) and (ii), or a styrene resin and (ii) such as a blended composition of polystyrene and polyphenylene ether; polyethylene or polybutene-1 and a polyphenylene ether; or polystyrene with a wholly aromatic polyester, e.g., from resorcinol and terephthaloyl chloride.

Among the preferred features of this invention are compositions where a polymer (b) is a polymerization product of at least one aliphatic ethylenically unsaturated monomer and is selected from polyethylene and other polyolefins and copolymers of such monomers, for example, polyethylene poly(methylene),

normally solid copolymers of ethylene and butene-1, copolymers of ethylene and ethyl acrylate, or vinyl acetate, butadiene-acrylonitrile copolymers, ionomers, poly(methyl methacrylate), polyisobutylene rubbers poly(vinyl chloride), poly(vinylidene chloride), a copolymer of vinyl chloride with vinyl acetate, natural rubber, a rubbery copolymer of butene-1 and ethylene, and a rubbery copolymer of butadiene and acrylonitrile. All such polymers are commercially available or can be prepared by techniques well known to those skilled in the art. As to the copolymers and terpolymers, the proportions of the repeating units may vary broadly and will be selected to provide the desired characteristics, i.e., normally rubbery, or normally solid. In addition to the polymers illustrated above, other suitable polymerization products of aliphatic ethylenically unsaturated monomers include derivatives thereof, such as halogenated hydrocarbon polymers, chlorosulfonated polyhydrocarbons and polymerized carboxy-substituted butadiene.

Other preferred polymer (b) components are selected from polyacetal homopolymers, such as polyoxymethylene, polyacetal copolymers, such as those based on trioxane, polyphenylene ethers, such as poly(2,6-dimethyl-1,4-phenylene) ether, polysulfones, such as the condensation product of bisphenol-A and 4,4'-dichloro diphenyl sulfone, polyamides, such as poly-caprolactam, or the product of hexamethylenediamine and adipic acid, polyimides, e.g., the product of bismaleimido diphenyl methane and methylene dianiline, normally solid or normally rubbery polyorganosilixanes, such as polyalkyl or aryl-siloxanes, or combinations of the two, and copolymers of polyorganosiloxanes with vinyl aromatics, e.g., styrene, acrylic monomers, e.g., methyl methacrylate, or aromatic esters, e.g., aromatic carbonates or the reaction products of bisphenol-A and iso or terephthaloyl chloride, as well as siloxane-nitrogen copolymers containing amido, amideimido, and imide groups. All such polymers are either commercially available or can be made in ways known to those skilled in the art.

Also preferred are polymer components (b) which comprise mixtures of any of classes (i), (ii) and/or (iii). For example, one such mixture would comprise a high molecular weight composition which is a mixture of polystyrene or other styrene resin, including rubber modified polystyrenes (i) with a self-condensation product of 2,6-dimethylphenol, i.e., poly(2,6-dimethyl-1,4-phenylene)ether.

Especially preferred compositions within the scope of this invention are those in which the combination contains from 1 to 99 parts by weight, and preferably from 15 to 85 parts by weight, of a poly(alkylene terephthalate, isophthalate or mixed terephthalate and isophthalate), having from 3 to 10 carbon atoms in the alkylene group, and from 99 to 1, and preferably from 85 to 15 parts by weight of either a high molecular weight poly(methyl methacrylate); a polyethylene, preferably a high density polyethylene, an acetal copolymer; a polyamide; a polyphenylene ether resin or a polyphenylene ether resin in combination with a styrene resin; a normally solid copolymer of ethylene and butene-1; or a normally crystalline wholly aromatic polyester. The preferred polyester (a) is poly (1,4-butylene terephthalate).

All of the present combinations include, as an essential ingredient, 2 to 90% by weight, based on total composition of a reinforcing filler (c). In general, any reinforcement can be used, e.g., fibers, whiskers or platelets of metals, e.g. aluminum, iron or nickel, and non-metals, e.g., carbon filaments, silicates, asbestos, TiO_2 and titanate whiskers, glass flakes and fibers. It is to be understood that, unless the filler adds to the strength, stiffness and impact strength of the composition, it is only a filler and not a reinforcing filler as contemplated herein.

In particular, the preferred reinforcing fillers are of glass and it is preferred to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda free. This is known as "E" glass. However, other glasses are useful where electrical properties are not so important, e.g., the low soda glass known as "C" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. The filament diameters range from 0.00012 to 0.00075 inch, but this is not critical to the present invention.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled in turn to yarns, ropes or rovings, or woven into mats, are also not critical to the invention. However, in preparing the present compositions, it is convenient to use the filamentous glass in the form of chopped strands of from $\frac{1}{8}$" to 1" long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however,

because the best properties are exhibited by thermoplastic injection molded articles in which the filament lengths lie between 0.000005" and 0.125 (1/8)".

Preferably the sized filamentous glass reinforcement comprises from 5 to 50% by weight based on the combined weight of glass and polymers. Especially preferably the glass will comprise from 10 to 40% by weight based on the combined weight of glass and resin. Generally, for direct molding use, up to 60% of glass can be present without causing flow problems. However, it is useful also to prepare the compositions containing substantially greater quantities, e.g. up to 80—90% by weight of glass. These concentrates can then be custom blended with blends of resins that are not glass reinforced to provide any desired glass content of a lower value.

Because it has been found that certain commonly used flammable sizings on the glass, e.g., dextrinized starch or synthetic polymers, contribute flammability often in greater proportion than expected from the amount present, it is preferred to use lightly sized or unsized glass reinforcements in those compositions of the present invention which are flame retardant. Sizings, if present, can readily be removed by heat cleaning or other techniques well known to those skilled in the art.

It is a preferred feature of this invention also to provide flame retardant glass reinforced thermoplastic compositions, as defined above, wherein the polyester is normally flammable, the composition also including

(d) a flame retardant additive in a minor proportion but in an amount at least sufficient to render the polyester resin non-burning or self-extinguishing.

A preferred feature of the invention is a flame retardant composition as above defined, which also includes:

(e) a polytetrafluoroethylene resin in a minor proportion based on the composition but in an amount at least sufficient to render said polyester resin non-dripping, when burning.

When used herein the terms "non-burning", "self-extinguishing", and "non-dripping" are used to describe composites which meet the standards of ASTM test method D-635 and of the following test, hereinafter designated the SE (self-extinction test). A molded piece of about 2½" x ½" x ⅛" is formed from the composition. When this sample is supported vertically and ignited, if it does not form flaming droplets sufficient to ignite a piece of cotton held 12 inches beneath and extinguishes itself within an average of 5 seconds after each of two 10-second ignitions, the composition is given an SE rating of A. If the flame is extinguished within an average of 25 seconds but no greater than 30 seconds and no flaming droplets are formed, the material is given an SE rating of B. If the flame is extinguished within an average of 25 seconds and flaming droplets are formed, the material is given an SE rating of C. ASTM test D-635 for flammability comprises contacting the end of a horizontal specimen ½" by 5" and "thickness normally supplied" with a Bunsen burner flame for 25 seconds, and repeating if there is no ignition. If the specimen does ignite but does not continue burning to the 4" mark after the flame is removed, it is classified as "self-extinguishing by this test".

The Oxygen Index of LOI (Limiting Oxygen Index) is a direct measure of a product's combustibility, based on the oxygen content of the combustion atmosphere. Appropriate specimens are placed in a combustion chimney and the oxygen is reduced stepwise until the material no longer supports a flame. The LOI is defined as follows:—

$$\mathrm{LOI} = \frac{100 \times \text{percentage oxygen}}{\text{percentage nitrogen} + \text{percentage oxygen in combustion-supporting gas}}$$

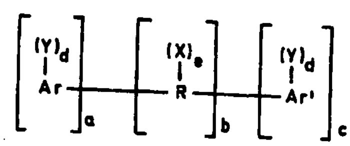
Further details of the Oxygen Index Test are found in ASTM test method D-2863. The compositions of this invention which contain flame-retardant additives in the specified amounts have a substantially higher oxygen index and thus are much less combustible than the controls.

The flame-retardant additives (d) which are used according to this invention are materials which are well known to those skilled in the art. Generally speaking, the more important of these compounds contain chemical elements employed for their ability to impart flame resistance, e.g., bromine, chlorine, antimony, phosphorus and nitrogen. It is preferred that the flame-retardant additive

comprise a halogenated organic compound (brominated or chlorinated); a halogen-containing organic compound in admixture with the antimony trioxide; elemental phosphorus (which in spite of its own flammability imparts flame-retardant properties to the compositions of this invention) or a phosphorus compound; a halogen-containing compound in admixture with a phosphorus compound or compounds containing phosphorus-nitrogen bonds or a mixture of two or more of the foregoing.

The amount of flame-retardant additive used is not critical to the invention, so long as it is present in a minor proportion based on said composition—major proportions will detract from physical properties—but at least sufficient to render the polyester resin-blend non-burning or self-extinguishing. Those skilled in the art are well aware that the amount will vary with the nature of the polymers in the blend and with the efficiency of the additive. In general, however, the amount of additive will be from 0.5 to 50 parts by weight per hundred parts of components (a) plus (b). A preferred range will be from 3 to 25 parts and an especially preferred range will be from 8 to 12 parts of additive per 100 parts of (a) + (b). Smaller amounts of compounds highly concentrated in the elements responsible for flame-retardance will be sufficient, e.g., elemental red phosphorus will be preferred at 0.5 to 2.0 parts by weight per hundred parts of (a) + (b), while phosphorus in the form of triphenyl phosphate will be used at 25 parts of phosphate per hundred parts of (a) + (b). Halogenated aromatics will be used at 2 to 20 parts and synergists, e.g. antimony trioxide, will be used at 1 to 10 parts by weight per 100 parts of components (a) plus (b).

Among the useful halogen-containing compounds are those of the formula



wherein R is an alkylene, alkylidene or cycloaliphatic linkage, e.g., methylene, ethylene, propylene, isopropylene, isopropylidene, butylene, isobutylene, amylene, cyclohexylene, or cyclopentylidene; a linkage selected from ether; carbonyl; amine; a sulfur-containing linkage, e.g., sulfide, sulfoxide, or sulfone; carbonate; or a phosphorus-containing linkage. R can also consist of two or more alkylene or alkylidene linkages connected by such groups as aromatic, amino, ether, ester, carbonyl, sulfide, sulfoxide, sulfone, or a phosphorus-containing linkage. R can be a dihydric phenol carbonate linkage, e.g., bisphenol –A carbonate linkage.

Ar and Ar′ are mono- or polycarbocyclic aromatic groups such as phenylene, biphenylene, terphenylene, or naphthylene. Ar and Ar′ may be the same or different.

Y is a substituent selected from organic, inorganic or organometallic radicals. The substituents represented by Y include (1) halogen, e.g., chlorine, bromine, iodine, or fluorine or (2) hydroxyl or ether groups of the general formula OE, wherein E is a monovalent hydrocarbon radical as defined below for X or (3) monovalent hydrocarbon groups as defined below for X or (4) other substituents, e.g., nitro or cyano, said substituents being essentially inert provided there be at least one and preferably two halogen atoms per aryl, e.g., phenyl, nucleus.

X is a monovalent hydrocarbon group exemplified by the following: alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, or decyl; aryl groups, such as phenyl, naphthyl, biphenyl, xylyl, or tolyl; aralkyl groups, such as benzyl, or ethylphenyl; cycloaliphatic groups, such as cyclopentyl, or cyclohexyl; as well as monovalent hydrocarbon groups containing inert substitutents therein. It will be understood that where more than one X is used they may be alike or different.

The letter *d* represents a whole number ranging from 1 to a maximum equivalent to the number of replaceable hydrogens substituted on the aromatic rings comprising Ar or Ar′. The letter *e* represents 0 or a whole number ranging from 1 to a maximum controlled by the number of replaceable hydrogens on R. The letters *a*, *b*, and *c* represent 0 or whole numbers. When *b* is not 0, neither *a* nor *c* may be 0. Otherwise either *a* or *c*, but not both, may be 0. Where *b* is 0, the aromatic groups are joined by a direct carbon-carbon bond.

The Y substituents on the aromatic groups, Ar and Ar′ can be varied in the *ortho*, *meta* or *para* positions on the aromatic rings and the groups can be in any

possible geometric relationship with respect to one another.

Included within the scope of the above formula are di-aromatics of which the following are representative:

2,2-bis-(3,5-dichlorophenyl)propane
bis-(2-chlorophenyl)methane
bis-(2,6-dibromophenyl)methane
1,1-bis-(4-iodophenyl)ethane
1,2-bis-(2,6-dichlorophenyl)ethane
1,1-bis-(2-chloro-4-iodophenyl)ethane
1,1-bis-(2-chloro-4-methylphenyl)ethane
1,1-bis-(3,5-dichlorophenyl)ethane
2,2-bis-(3-phenyl-4-bromophenyl)ethane
2,3-bis-(4,6-dichloronaphthyl)propane
2,2-bis-(2,6-dichlorophenyl)pentane
2,2-bis-(3,5-dichlorophenyl)hexane
bis-(4-chlorophenyl)phenylmethane
bis-(3,5-dichlorophenyl)cyclohexylmethane
bis-(3-nitro-4-bromophenyl)methane
bis-(4-hydroxy-2,6-dichloro-3-methoxyphenyl)methane
2,2-bis-(3,5-dichloro-4-hydroxyphenyl)propane
2,2-bis-(3-bromo-4-hydroxyphenyl)propane.

The preparation of these and other applicable biphenyls are known in the art. In place of the divalent aliphatic group in the above examples may be substituted sulfide, or sulfoxy.

Included within the above structural formula are substituted benzenes exemplified by tetrabromobenzene, hexachlorobenzene, hexabromobenzene, and biphenyls such as 2,2'-dichlorobiphenyl, 2,4'-dibromobiphenyl, 2,4'-dichlorobiphenyl, hexabromobiphenyl, octabromobiphenyl, decabromobiphenyl and halogenated diphenyl ethers, containing 2 to 10 halogen atoms.

The preferred halogen compounds for use as flame-retardant additives in accordance with this invention are aromatic halogen compounds such as chlorinated benzene, brominated benzene, chlorinated biphenyl, chlorinated terphenyl, brominated biphenyl, brominated terphenyl or a compound comprising two phenyl radicals separated by a divalent alkylene group and having at least two chlorine or bromine atoms per phenyl nucleus, and mixtures of at least two of the foregoing.

Especially preferred are hexabromobenzene and chlorinated biphenyls, alone, or mixed with antimony trioxide.

In general, the preferred phosphate compounds are selected from elemental phosphorus or organic phosphonic acids, phosphonates, phosphinates, phosphonites, phosphinites, phosphine oxides, phosphines, phosphites or phosphates. Illustrative are triphenyl phosphine oxide. This can be used alone or mixed with hexabromobenzene or a chlorinated biphenyl and, optionally, antimony trioxide.

Typical of the preferred phosphorus compounds to be employed in this invention would be those having the general formula

$$QO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OQ}{|}}{P}}-OQ$$

where each Q represents the same or different radicals including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, alkyl substituted aryl and aryl substituted alkyl; halogen; hydrogen and combinations thereof provided that at least one of said radicals Q is aryl. Typical examples of suitable phosphates include, phenylbisdodecyl phosphate, phenylbisneopentyl phosphate, phenylethyl hydrogen phosphate, phenyl-bis-(3,5,5'-trimethylhexyl) phosphate, ethyldiphenyl phosphate, 2-ethylhexyl di(p-tolyl) phosphate, diphenyl hydrogen phosphate, bis(2-ethylhexyl) p-tolylphosphate, tritolyl phosphate, bis(2-ethylhexyl)phenyl phosphate, tri(nonylphenyl)phosphate, phenylmethyl hydrogen phosphate, di(dodecyl) p-tolyl phosphate, tricresyl phosphate, triphenyl phosphate, halogenated triphenyl

phosphate, dibutylphenyl phosphate, 2-chloro-ethyldiphenyl phosphate, p-tolyl bis(2,5,5'-trimethylhexyl)phosphate, 2-ethylhexyldiphenyl phosphate, and diphenyl hydrogen phosphate. The preferred phosphates are those where each radical Q is aryl. The most preferred phosphate is triphenyl phosphate. It is also preferred to use triphenyl phosphate in combination with hexabromobenzene and, optionally, antimony trioxide.

Also suitable as flame-retardant additives for use in accordance with this invention are compounds containing phosphorus-nitrogen bonds, such as phosphonitrilic chloride, phosphorus ester amides, phosphoric acid amides, phosphonic acid amides, phosphinic acid amides, tris(aziridinyl)phosphine oxide or tetrakis(hydroxymethyl)phosphonium chloride. These flame-retardant additives are commercially available.

The polytetrafluoroethylene resins used in accordance with this invention as dripping retarding agents (e) are commercially available or can be prepared by known processes. They are white solids obtained by free radical initiated polymerization of tetrafluoroethylene in aqueous media with free radical catalysts, e.g., sodium, potassium or ammonium peroxydisulfates at 100 to 1000 psi. at 0—200°C. and preferably at 20—100°C. See Brubaker, U.S. Patent No. 2,393,967. While not essential, it is preferred to use the resins in the form of relatively large particles, e.g., of average size 0.3 to 0.7 mm., mostly 0.5 mm. These are better than the usual polytetrafluoroethylene powders which have particles of from 0.05 to 0.5 millimicrons in diameter. It is especially preferred to use the relatively large particle size material because it tends to disperse readily in polymers and bond them together into fibrous networks. Such preferred polytetrafluoroethylenes are designated by ASTM as Type 3, and are available commercially for general use in the extrusion of thin-walled tubular goods and tape.

The amount of polytetrafluoroethylene to be used can vary widely, from an amount at least sufficient to render the polyester non-dripping (when burning) but usually will be from 0.1 to 10 parts and preferably from 0.5 to 2.5 parts by weight per hundred parts by weight of the combination of components (a) + (b).

The reinforcements are added in any usual manner, e.g., by dry mixing or by mixing in the melted state in an extruder, on a heated mill or in other mixers.

By way of illustration, glass roving (a bundle of strands of filaments) is chopped into small pieces, e.g., ⅛" to 1" in length and put into an extrusion compounder with the polyester resin, (a), the co-blending polymer (b) and, if used, the flame retardant additive (d) and polytetrafluoroethylene (e) to produce molding pellets. The fibers are shortened in the process, coming out at less than 1/16" long. In another procedure, glass filaments are ground or milled to short lengths, and are mixed with the polyester resin, co-blending polymer and, optionally, flame retardant additive and polytetrafluoroethylene resin, by dry blending then either fluxed on a mill and ground, or they are extruded and chopped. In still another procedure continuous lengths of glass roving are drawn through a bath of melted polyester resin, the co-blending, second polymer and, optionally, the flame retardant additive and polytetrafluoroethylene resin, which procedure coats the filaments, and then the resin-coated glass strand is comminuted into pellets to form a molding compound. The glass fibers can also be mixed with resin and additives and directly molded, e.g., by injection or transfer molding techniques.

It is always very important to thoroughly free all of the ingredients, polyester resin, co-blending polymer, reinforcing filler, and flame retardant additives, from as much water as possible.

In addition, compounding should be carried out to ensure that the residence time in the machine is short; the temperature is carefully controlled; the frictional heat is utilized; and an intimate blend between the resin and the additives is obtained.

Although it is not essential, best results are obtained if the ingredients are precompounded, pelletized and then molded. Precompounding can be carried out in conventional equipment. For example, after carefully pre-drying the polyester resin, the co-blending polymer and other additives, and the reinforcement, e.g., under vacuum at 100°C. for 12 hours, a single screw extruder is fed with a dry blend of the ingredients, the screw employed having a long transition section to ensure proper melting. On the other hand, a twin screw extrusion machine, e.g., a 28 mm. Werner Pfleiderer machine can be fed with resins and additives at the feed port and reinforcement down stream. In either case, a generally suitable machine temperature will be 350 to 700°F.

The precompounded composition can be extruded and cut up into pieces of the size conventionally forming moulding compositions, such as conventional granules or pellets by standard techniques.

The compositions can be molded in any equipment conventionally used for reinforced thermoplastic compositions. For example, with poly(1,4-butylene terephthalate), good results will be obtained in an injection molding machine, e.g., of the Newbury type, with conventional cylinder temperatures, e.g., 500°F. and conventional mold temperatures, e.g., 150°F. If necessary, depending on the molding properties of the co-blending polymer, the amount of reinforcing filler and the rate of crystallization of the polyester component, those skilled in the art will be able to make the conventional adjustments in molding cycles to accommodate the composition. Typical conditions for a wide variety of materials will be exemplified hereinafter.

The following examples illustrate the invention. They are set forth as a further description, but are not to be construed as limiting the invention thereto.

EXAMPLES 1—3.

The following ingredients are dried in a vacuum at 100°C. for 10 hours:

poly(1,4-butylene terephthalate), m.p., 232°C., intrinsic viscosity: 0.65—0.75 dl/g.,

poly(methyl methacrylate), density 1.17—1.2 g./cc., and

fibrous glass reinforcement, ⅛",

The dry blends are extruded and moulded between 470 and 520°F. into test bars measuring ⅛" x ½" x 2½".

The test bars are tested for the following physical properties: Tensile Strength and elongation, ASTM D-638; Flexural strength and modulus, ASTM D-790; Impact strength, ASTM D-256; Heat distortion temperature, ASTM D-648.

The formulations used and the results obtained are set out in Table 1:

Table 1.

Physical Properties of Reinforced Polyester-Poly(methyl methacrylate) Compositions

Example	1A	1	2	3
Ingredients				
poly(1,4-butylene terephthalate)	0	20	40	60
poly(methyl methacrylate)	80	60	40	20
⅛" fibrous glass reinforcement	20	20	20	20
Properties				
Heat Distortion temp., °F. at 264 psi	194	192	320	311
Flexural modulus, psi	660,000	811,000	851,000	750,000
Impact Strength, ft.lbs./in. notch	1.1	1.1	1.2	1.3

Thus, a composition comprising two polymers and a glass reinforcement is seen to be highly useful. Blends containing equal amounts of polyester and polymethacrylate show a surprising increase in heat distortion temperature, a maintenance of good impact strength and a very high flexural modulus.

EXAMPLES 4—6.

The following ingredients are dried:

poly(1,4-butylene terephthalate) as in Example 1;

polyethylene, high density, 0.940—0.965 g./cc., (containing about 4% of butene-1); and

fibrous glass reinforcement, ⅛"

The dry blends are extruded and molded at 520°F. into test pieces and tested for physical properties.

The formulations used and the results obtained are set out in Table 2:

Table 2.

Physical Properties of Reinforced Polyester-Polyethylene Compositions

Example				
Ingredients (parts by weight)	4A	4	5	6
poly(1,4-butylene terephthalate)	0	20	40	60
polyethylene	80	60	40	20
⅛" fibrous glass reinforcement	20	20	20	20
Properties				
Heat distortion temp., °F. at 264 psi.	212	235	262	392
Flexural modulus, psi	273,000	275,000	311,000	348,000
Impact strength, notched, ft.-lbs./inch	2.7	1.7	1.5	1.2

When the formulation comprises equimolar amounts of polyester and polyethylene, a high heat distortion temperature and good notched impact strength were obtained. Also, as the amount of polyester is increased, both the modulus and the heat distortion temperatures increase.

EXAMPLE 7.

The following ingredients are dried:
poly(1,4-butylene terephthalate), as in Example 1;
acetal copolymer, density, 1.40 g./cc., (Celcon, manufactured by the Celanese Company); and
fibrous glass reinforcement, as in Example 1.

The dry blend is melt blended on a two-roll mill and compression molded at 220—230°C. The formulations used and the results obtained are set out in Table 3:

Table 3.

Physical Properties of Reinforced Polyester-Acetal Copolymer Compositions

Example	7A	7
Ingredients (parts by weight)		
poly(1,4-butylene terephthalate)	0	40
acetal copolymer	80	40
fibrous glass reinforcement	20	20
Properties		
Heat Distortion temp., °F. at 264 psi.	304	313
Modulus, psi.	600,000	570,000

The composite according to this invention has an increased heat distortion temperature in comparison with the reinforced acetal copolymer alone.

EXAMPLES 8 to 13.

The following ingredients are dried:
poly(1,4-butylene terephthalate), as in Example 1;
polyamide resin, nylon 6/10, density, 1.09 g/cc. (Zytel 31, manufactured by DuPont Company, "Zytel" is a Registered Trade Mark);
polyamide resin, nylon 6, density, 1.12—1.14 g/cc.; and
fibrous glass reinforcement, as in Example 1.

The dry blends of nylon 6/10 are melt blended on a two-roll mill at 210—220°C. and compression molded at 230°C. The dry blends of nylon 6 are extrusion blended at 520°F. The formulations used and the results obtained are set out in Table 4:

Table 4.

Physical Properties of Reinforced Polyester-Polyamide Compositions

Example	8A	8	9	10
Ingredients (parts by weight)				
poly(1,4-butylene terephthalate)	0	20	40	60
polyamide, nylon 6	80	60	40	20
$\frac{1}{8}$" fibrous glass reinforcement	20	20	20	20
Properties				
Heat distortion temp., ° F. at 264 psi	379	383	410	406
Flexural strength, psi.	6,700	8,400	7,100	5,700
Modulus, psi.	178,000	330,000	500,000	530,000
Impact strength, ft.-lbs./in. notch	3.6	2.0	1.5	1.3

As nylon 6 is blended into the polyester, easier processing is obtained. At the 60:20 ratio of nylon to polyester, the modulus increases sharply. This is also true of the 40-40 blend.

Table 4 (continued).

Physical Properties of Reinforced Polyester-Polyamide Compositions

Example	11A	11	12	13
Ingredients (parts by weight)				
poly(1,4-butylene terephthalate	0	20	40	60
polyamide, nylon 6/10	80	60	40	20
⅛" fibrous glass reinforcement	20	20	20	20
Properties				
Heat distortion temp., °F. at 264 psi	408	414	400	421
Flexural strength, psi.	14,000	14,300	6,000	5,200
Modulus, psi.	400,000	447,000	455,000	356,000
Impact strength, ft.-lbs./in. notch	1.2	1.4	1.4	2.3

Improved processing is obtained at the 60-20 blend of polyester and polyamide with increased impact strength and heat distortion temperature.

EXAMPLES 14 to 16.

The following ingredients are dried:

poly(1,4-butylene terephthalate), as in Example 1;

composition comprising poly(2,6-dimethyl-1,4-phenylene) ether and rubber modified, high impact polystyrene, equal parts density, 1.05—1.10; and

fibrous glass reinforcement, ⅛ inch, (P 158 B, manufactured by Owens Corning Fiberglas Corp.).

The dry blends are melt blended by extrusion at 460—520°F. and molded at 520°F. The formulations used and the results obtained are set out in Table 5:

Table 5.

Physical Properties of Reinforced Polyester-Polyphenylene Ether Compositions

Examples	14	15	16
Ingredients (parts by weight)			
poly(1,4-butylene terephthalate)	20	40	60
polyphenylene ether	30	20	10
polystyrene (rubber modified)	30	20	10
⅛" fibrous glass reinforcement	20	20	20
Properties			
Heat distortion temp., °F. at 264 psi	260	298	395
Tensile strength, psi.	6,040	6,400	7,500
Flexural modulus, psi.	474,000	580,000	620,000
Impact strength ft.-lbs./inch, notch	1.1	1.2	1.7

Improved extrusion is noticed as the amount of polyester is increased. In addition the composites according to this invention have a smoother molded surface than those containing no polyester. Good impact strengths are obtained with 10:10:60 polystyrene-polyphenylene ether-polyester combinations along with very high heat distortion temperature and flexural modulus. The procedure is repeated, substituting for the polyphenylene ether-styrene resin composition, an unmodified poly(2,6-dimethyl-1,4-phenylene)ether, (PPO, manufactured by General Electric Co.). Compositions according to this invention are obtained.

EXAMPLE 17.

A dry blend of 60 parts by weight of poly(1,4-butylene terephthalate), 20 parts by weight of an (85-15 p-phenylene isophthalate terephthalate) wholly aromatic polyester, prepared according to U.S. Patent No. 3,036,990, and 20 parts by weight of fibrous glass reinforcement, as in Example 1 is milled at 240°C. and heated at 300°C. provide a moldable reinforced composition according to this invention.

EXAMPLES 18 to 22.

The following ingredients are dried:
poly(1,4-butylene terephthalate), as in Example 1;
polyethylene, as in Example 4;
fibrous glass reinforcement, as in Example 4;
highly chlorinated biphenyl (chlorine content 59%, softening point 98—105°C);
hexabromobenzene;
triphenyl phosphate;
antimony trioxide; and
polytetrafluoroethylene resin (ASTM Type 3, particle size 0.3—0.7 mm.)

The blends are compounded and molded according to the procedure of Example 1. The formulations used are set out in Table 6:

Table 6.

Flame Retardant Reinforced Polyester-Polyethylene Compositions

Examples / *Ingredients* (parts by weight)	18	19	20
poly(1,4-butylene terephthalate)	20	20	20
polyethylene	60	60	60
fibrous glass reinforcement	20	20	20
chlorinated biphenyl	10	—	—
hexabromobenzene	—	7	—
triphenyl phosphate	—	—	7
antimony trioxide	4	3	—
polytetrafluoroethylene resin	1.0	1.5	1.0

Table 6.

Flame Retardant Reinforced Polyester-Polyethylene Compositions (continued)

Examples	21	22
Ingredients (parts by weight)		
poly(1,4-butylene terephthalate)	20	20
polyethylene	60	60
fibrous glass reinforcement	20	20
chlorinated biphenyl	20	—
hexabromobenzene	—	10.5
triphenyl phosphate	—	—
antimony trioxide	8	4.5
polytetrafluoroethylene resin	1.0	1.5

Flame retardant, non-dripping compositions according to this invention are obtained.

EXAMPLE 23.

The procedure of Example 4 is repeated, substituting for the poly(1,4-butylene terephthalate), the following high molecular weight, rapidly crystallizable linear polyesters:

a 70/30 1,4-butylene terephthalate-1,4-butylene isophthalate polyester;

poly(1,3-propylene terephthalate) prepared from trimethylene glycol and dimethyl terephthalate by the procedure of U.S. Patent No. 2,465,319, Example 12; and

poly(hexamethylene terephthalate) prepared from hexamethylene glycol and dimethyl terephthalate by the procedure of U.S. Patent No. 2,465,319, m.p., 154°C.

Reinforced compositions according to this invention are obtained.

Obviously, other modifications of the present invention are possible in light of the above teachings.

For example, reinforced compositions according to this invention are obtained if, instead of polyethylene in Example 4, there are substituted:

poly(4-methyl pentene-1), density 0.83 g./cc. (manufactured by Imperial Chemical Industries);

a copolymer of ethylene and ethyl acrylate, density, 0.925—0.950 g./cc.;
poly(vinyl chloride), density 1.35—1.45 g./cc.;
poly(vinyl chloride—vinyl acetate), density 1.35—1.45 g./cc.;
poly(vinylidene chloride), density 1.65—1.72 g./cc.;
natural rubber; and
a rubbery copolymer of butadiene (83%) and acrylonitrile (18%).

In addition, there can be substituted for polyethylene in Example 4:

a polyacetal homopolymer, density 1.42 g./cc.;

a polysulfone, density, 1.24 g./cc., (Bakelite P 1700 manufactured by Union Carbide—Bakelite is a Registered Trade Mark);

a polyamide; a polyorganosiloxane;

copolymers of a polyorganosiloxane with, respectively, styrene, methyl methacrylate and the reaction product of bisphenol-A and isophthaloyl chloride; and

a siloxane-nitrogen copolymer containing amido, amide-imido or imide groups.

The procedure of Example 4 can be repeated, substituting for glass fibers, the following reinforcing fillers:

aliminum powder;
bronze powder;
silicate;
ceramic fibers;
titanate fibers;
fumed colloidal silica;
asbestos fibers;
quartz; and
carbon black.

Reinforced composites according to this invention are obtained.

Because of their excellent physical, mechanical, chemical, electrical and thermal properties and the enhanced flame resistance of certain embodiments, the reinforced polyester-coblending polymer composites of this invention have many and varied uses. The formulations may be used alone as molding powders or mixed with other polymers and may contain various additional, non-reinforcing fillers, such as wood flour, cloth fibers and clays, as well as pigments and dyes, stabilizers and plasticizers.

WHAT WE CLAIM IS:—

1. A reinforced thermoplastic composition that is rigid at temperatures of up to 90°F, which comprises a homogeneous crystalline normally rigid, reinforceable mixture of:

(a) at least one high molecular weight normally crystalline polyester resin which rapidly crystallizes from the melt (as hereinbefore defined);

(b) at least one high molecular weight normally crystalline, normally amorphous or normally partially crystalline and partially amorphous polymer of:

(i) at least one aliphatic ethylenically unsaturated monomer excluding propylene;

(ii) at least one difunctionally reactive compound which is polymerizable by self-condensation; and/or

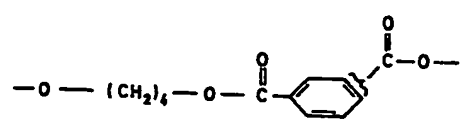
(iii) at least two difunctionally reactive compounds which are polymerizable by polycondensation;

in the concentration range of from 1 to 99 parts by weight of (a) to 99 to 1 parts by weight of (b); and

(c) from 2 to 90% by weight, based on total composition, of a reinforcing filler for said homogeneous, crystalline, normally rigid, reinforceable mixture; and when plolymer (b) is a polyester, it is a wholly aromatic polyester and different from polyester (a).

2. A composition as defifned in Claim 1 wherein said polyester resin (a) is a poly(alkylene terephthalate, isophthalate or mixed terephthalate and isophthalate), said alkylene groups containing from 3 to 10 carbon atoms.

3. A composition as defined in Claim 1 wherein polyester resin (a) includes repeating units of the formula:



4. A composition as defined in Claim 3 wherein said polyester (a) is poly(1,4-butylene terephthalate).

5. A composition as claimed in any preceding claim wherein said polymer (b) is a polymerization product of at least one aliphatic ethylenically unsaturated monomer and is

polyethylene,
poly(methyl methacrylate)
poly(methylpentene),
a copolymer of ethylene and ethyl acrylate,
poly(vinyl chloride),
poly(vinylidene chloride),
a copolymer of vinyl chloride and vinyl acetate, natural rubber, or
a rubbery copolymer of butadiene and acrylonitrile.

6. A composition as defined in any of Claims 1 to 4 wherein said polymer (b) is
a polyacetal,
an acetal copolymer,
a polyphenylene ether,
a polysulfone,
a polyamide,
a polyimide,
a polyorganosiloxane,
a copolymer of a polyorganosiloxane and a vinyl aromatic monomer, an acrylic monomer or an aromatic ester, or
a siloxane-nitrogen copolymer containing amido, amide-imido or imide groups.

7. A composition as defined in any of claims 1 to 4 wherein said ethylenically unsaturated monomer is styrene and said difunctionally reactive compound is 2,6-dimethylphenol.

8. A composition as defined in Claim 1 wherein said reinforcing filler (c) is a reinforcing metal, ceramic, silica, quartz, glass or carbon.

9. A composition as defined in Claim 8 wherein said reinforcing filler is filamentous glass.

10. A composition as defined in any preceding claim wherein said polyester resin is normally flammable, and the composition also includes
(d) a flame retardant additive in a minor proportion but in an amount at least sufficient to render said polyester resin non-burning or self-extinguishing.

11. A composition as defined in Claim 10 which comprises:
(e) a polytetrafluoroethylene resin in a minor proportion based on said composition but in an amount at least sufficient to render said polyester resin non-dripping, when burning.

12. A composition as defined in Claim 10 or 11 wherein said flame retardant additive is a halogen-containing compound; a halogen-containing compound in admixture with antimony trioxide; elemental phosphorus, an organic phosphonic acid, a phosphonate, phosphinate, a phosphonite, a phosphinite, a phosphine oxide, a phosphine, a phosphite, a phosphate or a mixture of any of the foregoing.

13. A composition as defined in Claim 12 wherein said flame retardant additive is triphenyl phosphate.

14. A composition as defined in Claim 12 wherein said flame retardant additive is chlorinated benzene, brominated benzene, chlorinated biphenyl, chlorinated terphenyl, brominated biphenyl, brominated terphenyl, a compound comprising two phenyl radicals separated by an alkylene group or oxygen atom and having at least two chlorine or bromine substituents per benzene ring, or a mixture thereof.

15. A composition as defined in Claim 1 substantially as hereinbefore described.

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